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Catalytic decomposition of Nitrous Oxide
Final Report

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1. INTRODUCTION

This report details the work undertaken by SSTL for EOARD under contract number F61775-01-WE017, (reference number SPC 01-4017). Additional data and analysis covering additional tests carried out between the original submission in July 2002 and June 2003 has been incorporated.

This report summarises the efforts to develop a prototype nitrous oxide monopropellant thruster for small satellite applications.

Abbreviations used in this report are as follows:

RGA	Residual Gas Analysis
SEM-EDX	Scanning Electron Microscope - Energy Dispersive X-ray spectrometry
UniS-CD	University of Surrey – Chemistry Department
XPS	X-ray Photoelectron Spectroscopy

2. SUMMARY OF WORK UNDERTAKEN

The following work has been undertaken in support of the program

- Manufacture of a prototype thruster, as detailed in the Interim Report, has been completed.
- A test plan including basic operating parameters (see section 3.2) to allow catalytically initiated decomposition of nitrous oxide has been developed.
- A series of tests using Shell 405 catalyst, designed for hydrazine have demonstrated that, with initial catalyst heating to around 300°C, appreciable catalytic decomposition of nitrous oxide can be initiated. Silica fibre felt thermal insulation was required to maximise decomposition temperature. Decomposition temperatures in excess of 750°C were recorded, although the actual temperatures may have been considerably higher.
- However catalyst degradation was such that catalytic activity ceased after only one decomposition trial resulting in high temperature. Degradation took the form of significant Iridium metal loss, and alteration of the surface distribution of iridium metal.
- The University of Surrey have manufactured a rhodium metal catalyst on an alumina substrate (Rh catalyst) as an alternative to the commercial Shell 405. Theoretical evaluation suggests that that Rh catalysts could increase the rate of nitrous oxide decomposition per metal atom of catalyst, and enable a reduced temperature / heat input for catalyst activation.
- Testing of this catalyst has indicated that it must be heated to 400°C to commence catalytic decomposition of N₂O, and that decomposition temperatures in excess of 1100°C can be achieved. It is believed that a lower activation temperature and a higher steady state decomposition temperature are feasible with an improved catalyst.
- The Rh catalyst has achieved at least 5 restarts (corresponding to a total N₂O throughput of 500g, 3x that measured for Shell 405), compared to none for the Shell 405. Degradation is thought to occur by a combination of active metal loss and structural collapse of the alumina support.
- A programme of further work covering catalyst development, further decomposition chamber testing and design improvements, and prototype flight thruster tests in a representative flight environment is suggested.

3. EXPERIMENTAL PROGRAMME

3.1 Test setup

Experimental objectives were to:

- Determine a suitable catalyst and set of operating conditions which would provide a high operating temperature, decomposing the N₂O at the highest temperature compatible with the materials constraints imposed by use of off-the-shelf materials, specifically a stainless steel reaction chamber.
- Use minimal input power to initiate and sustain decomposition.
- Define the ability of the catalyst to sustain restarts, i.e. its degradation after repeated use.

The prototype thruster, detailed in the Interim Report, was designed to simulate as closely as possible a lightweight flight thruster made from low cost materials. However a bolted flange arrangement allowed nozzle removal and access to the catalyst (for replacement). In a flight thruster the catalyst would be welded inside the chamber, reducing the mass of the chamber reducing the thermal inertia, thus reducing heat loss from the catalyst bed and decomposed nitrous oxide.

The prototype thruster design parameters were:

Thrust	100mN
Specific impulse	150s
Mass flow rate of N ₂ O	0.1g/s
Chamber temperature (max / min / average)	918 / 683 / 800 °C
Operating pressure	3 Bar / 44.1psi
Power input to initiate decomposition	30W
Heating time to initiate decomposition	5-7min / 300-420s
Impulse	5000-7500Ns (equivalent to 3.3-5kg propellant at 150s Isp)

Table 3-1: Nitrous oxide monopropellant thruster design parameters

The schematic below shows the arrangement of test apparatus. The mass flow rate was measured by decanting a small quantity (~150g) of gaseous N₂O into a separate cylinder, which could be weighed during the test. This 'catch and weigh' method enabled more accurate monitoring of mass flow rate than using the SSTL in-house flow meter.

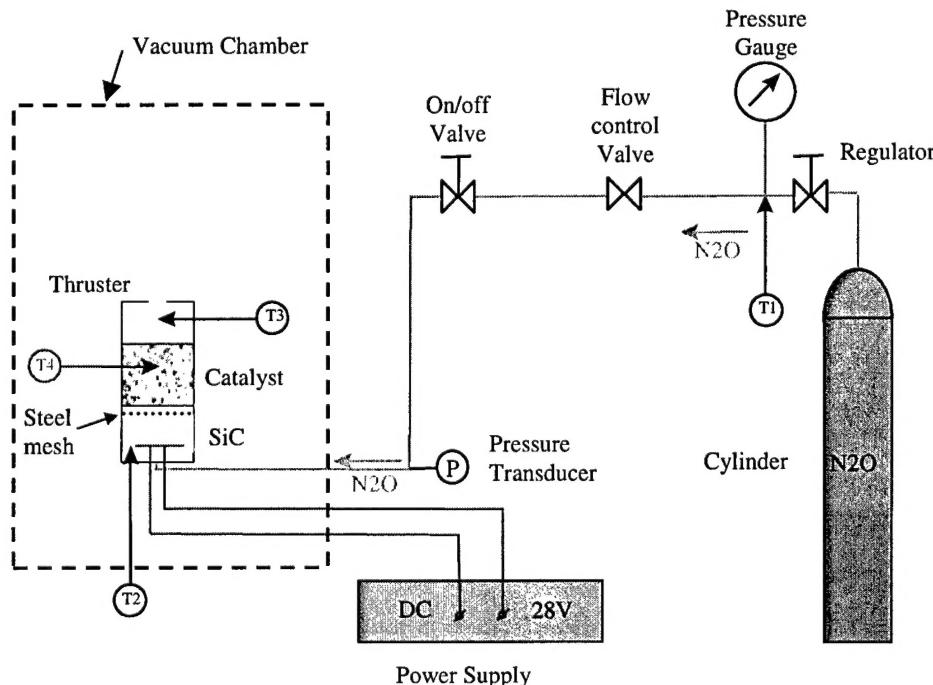


Figure 3.1: Schematic of test set-up for N₂O prototype thruster

A photograph of the laboratory test setup is shown in *Figure 3.2*, below:

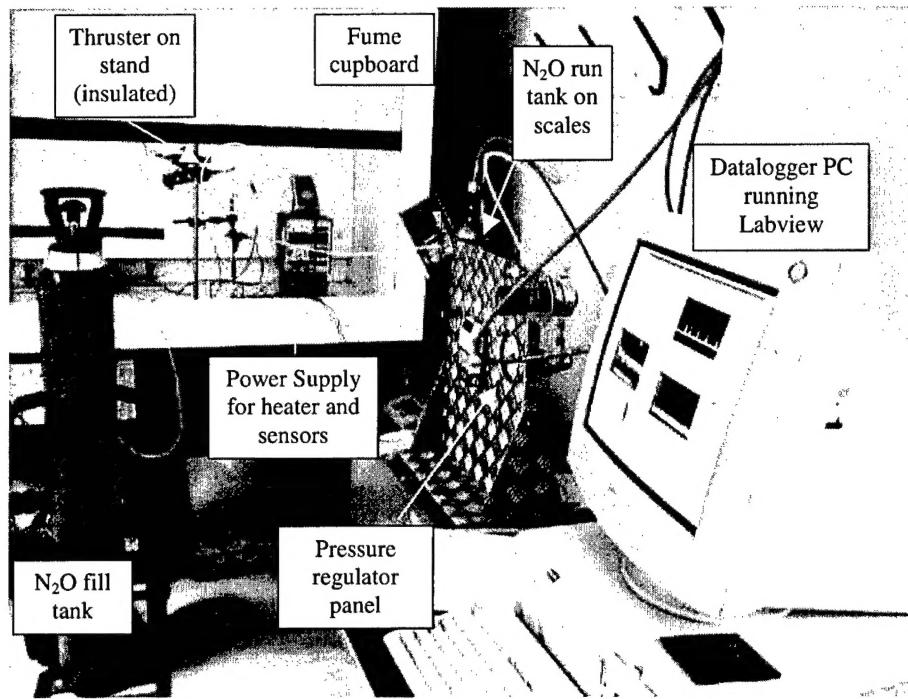
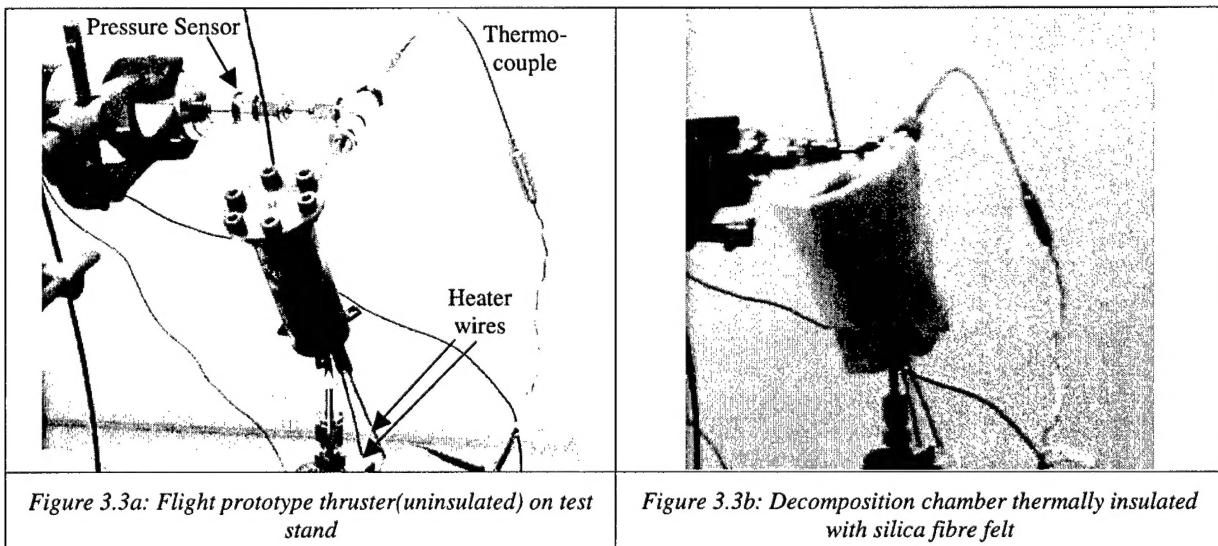


Figure 3.2: Laboratory layout for N₂O prototype thruster

A spiral wound heater rated to 30W and supplied by H&B sensors was brazed into the base of the thruster chamber. In initial tests the catalyst particles were placed in direct contact with the heater, filling ~2/3 of the chamber. Thermocouple T2 was mounted through Swagelock fittings so that the tip sat in the centre of the heater spiral adjacent to the heater. The uppermost 1/3 of the chamber was left empty and a thermocouple, indicated by T3 in *Figure 3.1*, was inserted to monitor the final decomposition temperature. This temperature is the one referred to in discussions as the chamber temperature. Later tests used a layer of SiC particles around the thruster, separated from the catalyst particles by fine steel mesh. This prevented direct thermal contact between the heater and the hot catalyst. The assembled prototype flight thruster is shown in *Figure 3.3*, below. The upper bolted flange containing the nozzle is 36mm diameter, and the decomposition chamber is 60mm long. Fittings were machined into the base to allow connection to a suitable interface, as per an actual flight system.



3.2 Basic operating parameters

The following variables were examined in the initial trials:

Input voltage / current	28V / 1.07A (~30W)
Heating time to initiate decomposition	300-460s
Total heating time	540-720s
Regulator pressure	0.6-2.2Bar above ambient (Barg)
Flow rate (N.B. not independent from regulator pressure)	0.05-0.14g/sec
Catalyst	Shell 405, 36wt% Ir on γ -Al ₂ O ₃ as a baseline

Table 3-2: Variables for N₂O prototype monopropellant thruster

The preferred operating parameters were found to be:

Input power	30W @28V
Heating time to initiate decomposition	600s (10minutes)
Total heating time	700s (11.5 minutes)
Regulator pressure	1Bar above ambient (Barg) Up to 3 Barg tested
Flow rate	0.1-0.14g/sec

Table 3-3: Preferred parameters for N₂O prototype monopropellant thruster

3.3 Test sequence

The chamber was manufactured from 300 series stainless steel. Initial test runs showed that wrapping the chamber in fibrous SIO₂ (rock wool) could significantly increase the decomposition temperature. The bulk fibre was supplied by RS Components.

A test under vacuum with and without insulation to determine the effect of convective cooling, and whether the insulation can be dispensed with in space is due to be carried out.

3.3.1 Tests 1-4:

A series of tests were carried out using the parameters in *Table 2*. ~15g of fresh Shell 405 was used. A maximum decomposition temperature of 720°C during Run 4 was measured by the thermocouple T3. The key parameters for this run were a flow control valve setting of 40, 4Bar indicated on the pressure regulator, 420s of heating time prior to flowing nitrous oxide and 645 s of total heating time. The parameter matrix for this run and the others is given in Appendix A. Test data from Run 4 is shown in *Figure 3.4*:

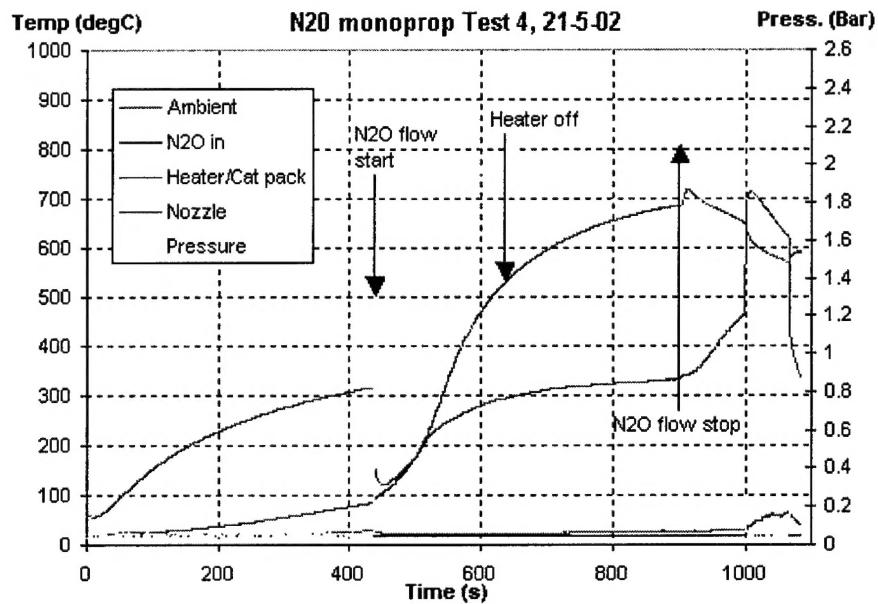


Figure 3.4: Test run 4, using Shell 405 catalyst

After run 4 the heater was found to have failed electrically, although no external damage was noted. It was believed that this may have stemmed from excessive heating by the catalyst bed. Given that the heater is rated for temperatures up to 950°C, this suggests that the internal temperatures may have been higher than the gas temperature upstream of the nozzle.

After the flow of nitrous oxide was stopped, conductive heat transfer ('soak-back') from the catalyst upstream to the heater may have increased (since the nitrous oxide flow carried heat from the heater towards the nozzle). This inference is supported by the temperature measurement at the heater/catalyst pack end of the chamber, which rose from around 330°C to 714°C after the nitrous oxide flow ceased (see brown 'Heater/Cat pack' trace on *Figure 3.4*, above). A nitrogen purge immediately after nitrous oxide flow cutoff was incorporated in the test procedure.

3.3.2 Tests 5-7

A single catalyst specimen g of ~0.5wt% Rh supported on a TiO₂ (Titania) coated Al₂O₃ (Alumina) ceramic foam block ~5mm x 5mm x 20mm provided by University of Surrey chemistry department was placed in the chamber instead of the Shell 405 particles. A peak decomposition temperature of 260°C was achieved, considerably lower than the temperature recorded using Shell 405. Two reasons may have caused this:

- 1) Low content of active metal on catalyst piece: Less than 0.5wt% Rh had been deposited, compared to ~36wt% Ir on the Al₂O₃ particles in Shell 405.
- 2) Poor thermal contact between heater and catalyst, stemming from geometry. The catalyst specimen also did not occupy the chamber cross section, allowing significant N₂O gas to bypass the catalyst and continue, unreacted to the nozzle

3.3.3 Tests 8-12

A fresh sample of ~15g Shell 405 was placed in the chamber, separated from the heater by a layer of 0.5mm (average size) SiC particles and a thin steel mesh. A maximum decomposition temperature of 751°C during Run 12 was measured by the thermocouple T3. Compared to Run 4, the only changed parameters were 3Bar indicated on the pressure regulator (v. 4Bar), and 720s of total heating time (v. 645s). A nitrogen purge was made immediately after cutoff of N₂O flow. The combination of the SiC layer between the heater and the catalyst particles and the nitrogen purge ensured that the heater temperature remained below 300°C at all times. Test data from Run 12 is shown in *Figure 3.5*.

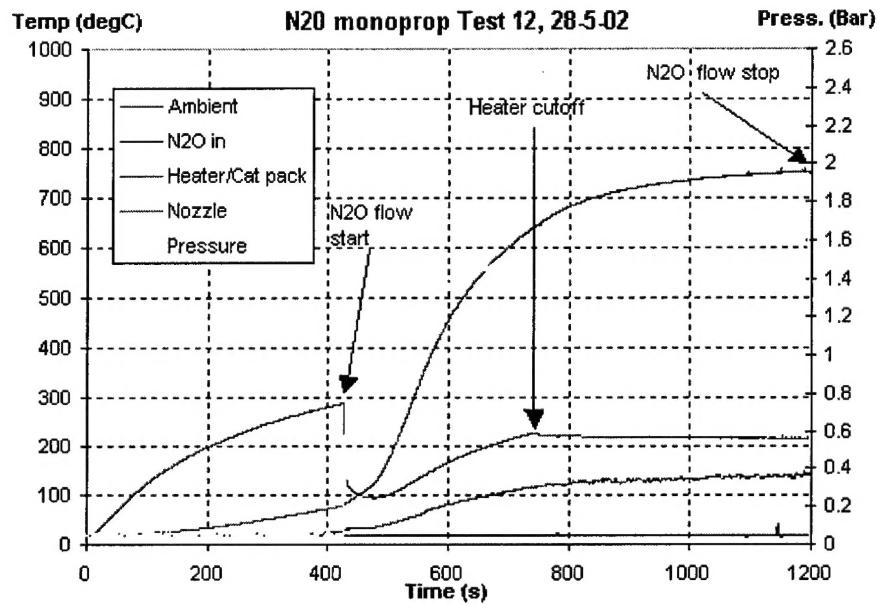


Figure 3.5: Test run 12, using Shell 405 catalyst

3.3.4 Tests 13-16

These tests compared the performance of the same catalyst sample under repeated heating and N₂O decomposition conditions, and are detailed in Section 3.4.4.

3.3.5 Tests 17-32

These tests utilised the University of Surrey fabricated Rh/Al₂O₃ catalyst. Objectives were

- Determine approximate catalytic decomposition parameters for comparison with Shell-405
- Determine survivability of catalyst, in terms of N₂O throughput before failure
- Establish mode of failure and suggest way forward.

4 CATALYST SELECTION AND TESTING

4.1 Overview

A range of catalysts were evaluated, with a view to identifying a catalyst with 1 or more of the following three qualities:

- 1) A catalyst easier to obtain than Shell 405 (US\$10,000/lb and requiring a US export license)
- 2) A more effective catalyst than Shell 405, in terms of the catalyst temperature required to initiate sustained N₂O decomposition
- 3) A more robust catalyst than Shell 405, in terms of the number of propellant runs which can be sustained prior to unacceptable catalyst degradation (with 'unacceptable' being defined as an inability to catalyse decomposition, resulting in peak temperatures of 200°C or less).

Vadim Zakirov in his Ph.D. thesis suggested the following catalysts:

- a. Mix of nickel oxide (NiO) pieces with nickel oxide coated zirconia (ZrO₂) pieces
- b. 0.3at% (2-3wt%) Rh deposited as Rh₂O₃ on 1.5mm diameter MgO+ZrO₂ spheres
- c. Shell 405, quoted as 5.5at% (equivalent to 36wt%) Ir on Al₂O₃

Another catalyst, produced by Vadim Zakirov and believed to be 3wt%Rh on 2.5mm diameter Al₂O₃ spheres was provided to the University of Surrey Chemistry Department (UniS-CD) for chemical and catalytic effectiveness characterisation. UniS-CD prepared 2 types of catalyst base on its earlier evaluation of Vadim Zakirov's material.

- 1) 0.5wt%Rh on a sol-gel coating of TiO₂ deposited on a single block of Al₂O₃ foam ~5x5x20mm, prepared as described below:

Add absolute ethanol (Hayman 99.99%), distilled water and hydrochloric acid (Aldrich 36%) to a closed reaction vessel, and then shake to ensure homogeneity. Ethanol and titanium isopropoxide (TiOP; Aldrich 97%), are then added slowly. The mixture is then left to stir for approximately 15 hours, followed by the remaining mixture of water and ethanol being added. The resulting mixture is allowed to mix for about 24 hours to ensure a clear, colourless, and homogeneous appearance. A clear wet gel then was allowed to gel over time, which is typically four-seven days, so induction of RhCl₃·H₂O into the structure is conducted between one-two days with constant stirring to ensure molecular homogeneity. A white-grey gel was produced. The gel is then dried at 373K to drive off the ethanol and water. After crushing and calcining the gel was ready for testing. The gel was formed due to condensation reactions, extensive cross-linking, and polymerisation which allowed the cross linking to occur. This developed a 3-dimension tetrahedral titania framework across the gel.

Deposition of the gel onto a ceramic foam catalyst was carried out as follows:

White Al₂O₃ ceramic foam (CF; Hi-Por alumina provided by Dytech Corporation Ltd) was acid etched (3M HNO₃, 200 cm³) three times for 15 h. A mixture of TiO₂ (SG, 16 cm³) and ethanol (4 cm³, 0.087 mol, Hayman 99.99 %) was surface coated on CF block (1 cm x 1 cm x 3 cm) and dried for 16h. RhCl₃·H₂O (0.0270 g, 0.118 mmol, Aldrich 99.99 %) was dissolved in ethanol (20 cm³, 0.434 mol, Hayman 99.99 %) and added to the TiO₂ (SG-80 %)/Al₂O₃ CF and dried at 313-343 K. The product was pink-red coloured ceramic block was then further dried at 373 K for 24h.

The catalyst deposited on a block of Al₂O₃ foam was not found to enable decomposition of N₂O, possibly due to the geometry of the foam block not being matched to the internal shape of the decomposition chamber, allowing gas to bypass it. An alternative was tried:

- 2) 5wt% Rh on 2.5mm Ø Al₂O₃ spheres (supplied by Johnson-Matthey corporation). The Rh was deposited using an impregnation method, starting with Rh (III) chloride hydrate crystals, supplied by Sigma-Aldrich corporation. After impregnation, the white Rh spheres were largely dark grey/black in colour, similar to the Shell 405 catalyst particles, with occasional (<5%) a lighter shade of grey.

This catalyst (referred to as 5wt% Rh on Al₂O₃) was used for the bulk of the tests, and is labelled as Rh-2, Rh-3 and Rh-4 in the test matrix in Appendix A.

4.2 Effectiveness of N₂O decomposition by residual gas analysis

Residual Gas Analysis (RGA) measures gaseous effluent of a reaction, in terms of partial pressures. The technique allows one to assess changes in the gaseous product before, during, and after reactions. Coupled to a mass spectrometry allows assessment of the nature of the product. For each reaction 40-70 mg of sample was used, weighed on a balance and placed onto a cotton wool support inside a silica micro-reactor, part of a Sensorlab RGA kit. Each sample was reduced under hydrogen for one hour to increase catalytic activity. The system was flushed by argon, and put onto bypass (this bypassed the reactor vessel but still entered the RGA) therefore allowing a stabilised recording of gaseous levels pre-reaction. During the reaction a profile may be obtained that can be referenced back to the bypass indicating catalytic activity. A flow rate of 30 ml min⁻¹ of N₂O for 20 minutes to ensure equilibrium was reached in the system previous to the reaction. A heat rate of 10K min⁻¹ was used up to 800°C. The following RGA peaks were observed:

m/z = 44 N₂O

m/z = 40 Ar

m/z = 32 O₂

The justification for only analysing three peaks, is in relation to their function and interest in the decomposition of N₂O. Ar was looked at as a reference or safety (due to Ar inertness it should stay at relatively constant partial pressure throughout the reaction). N₂O and O₂ were the only active gases to be analysed due to two reasons; (i) it is the N₂O decomposition that is the defining feature, therefore it is the change in this we are most interested in. O₂ was measured to confirm decomposition was occurring and producing appropriate decomposition products, (ii) and by reducing the number of products measured the greater number of data collections are made on the two concerned gases, therefore increasing accuracy of results.

To ensure that peaks observed were those of O₂ and N₂O a CO and a CO₂ monitor was attached to the reaction stream. This is due to the relative molecular mass of N₂/CO = 28, and NO₂/CO₂ = 44.

The overall procedure involved heating the catalyst sample to 800°C in a stream of 80% Ar and 20% N₂O at 100cc/min, equivalent to a mass flow rate of 0.036g/min at 25°C. A results plot is shown in *Figure 4.1* below:

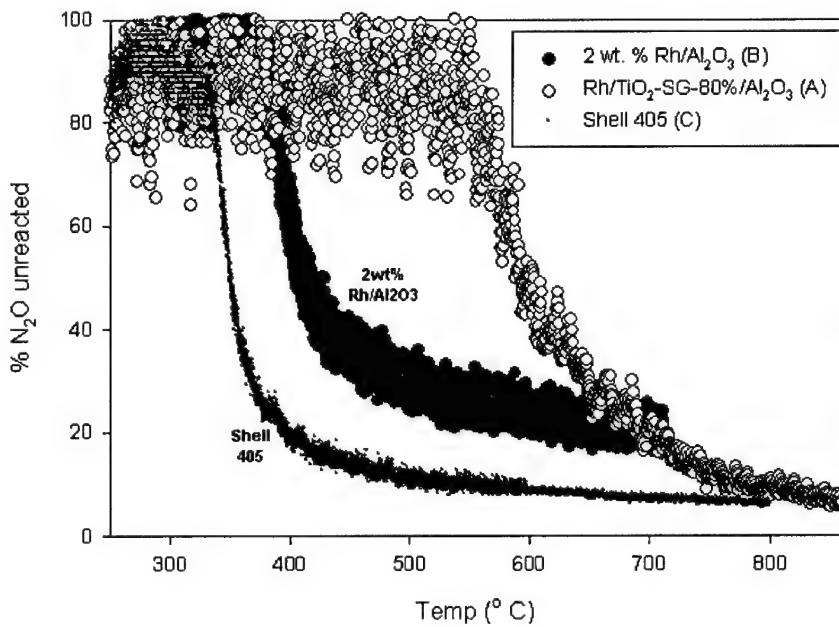


Figure 4.1: RGA analysis of three separate catalyst showing relative performance at decomposing N₂O.

RGA showed that ability of Shell 405 and the 2 wt% Rh on Al₂O₃ catalyst to decompose nitrous oxide was similar, starting around 350°C and completing by 500°C. The Rh / TiO₂ / Al₂O₃ catalyst produced by the sol-gel route however did not begin to decompose nitrous oxide until a temperature of almost 600°C was reached, with completion around 800°C. This high activation temperature could be an issue if used on a spacecraft with limited power, since the heating time and hence energy required prior to a firing would be the highest. However this catalyst contained <0.5wt% Rh metal, whereas the Rh on Al₂O₃ and Shell 405 catalysts contained 2-3wt% Rh and 36wt% of metal respectively. The active metal component is critical for catalysis so it is unsurprising that the SSC and Shell 405 catalysts were much more effective. All

three catalysts decomposed similar quantities of N₂O, provided a high enough temperature was reached. However this was at a much lower (~0.0006g/s) flow rate than would be experienced in a flight thruster (~0.1g/s), so high metal content would be preferred in a flight catalyst bed.

A better metric of catalyst effectiveness is given by the turnover frequency, TOF, which is defined as the number of O₂ molecules produced from N₂O per second per metal atom, at a standard temperature, 973K (700°C) in this case. TOF represents a fair comparison of the reactivity of a given metal catalyst/substrate combination, since catalysts as provided have different metal combinations and therefore cannot be directly compared for reactivity.

UniS-CD calculated the following data for turnover frequency, together with the activation energies for decomposition of N₂O:

	Catalyst	Activation energy (kJ/mol)	TOF for N ₂ O at 900K
1	Shell 405	205	0.15
2	Rh/Al ₂ O ₃ provided by Vadim Zakirov (SSC)	241	0.48
3	0.5wt% Rh on TiO ₂ (Degussa IMP)	50	0.78
4	0.5wt% Rh on TiO ₂ (SG)	159	9.27
5	0.5wt% Rh on TiO ₂ deposited by SG on Al ₂ O ₃ ceramic foam (Uni. Surrey)	217	9.27

Table 4-1: Effectiveness of different metal /substrate catalyst types as measured by turnover frequency

SG refers to a sol-gel route used to form the TiO₂ substrate, IMP to a wetness impregnation technique used to deposit the active metal catalyst component on the substrate. Catalyst 4 was made using both sol-gel and impregnation routes. In comparison, catalyst 3 was made using TiO₂ substrate particles supplied by Degussa, with Rh subsequently deposited on these.

Rh on TiO₂ would appear, from a calculation perspective, to be a more effective N₂O catalyst than Shell 405. However this takes no account of the catalyst stability, nor of the relative effects of the substrate v. the active metal ingredient.

4.3 Chemical/visual analysis of catalyst

The Shell 405 catalyst consisted of a number of black, irregular shaped granules about 1-2mm in each dimension. The 5wt% Rh on Al₂O₃ catalyst produced by UniS-CD and tested in the prototype decomposition chamber had the appearance of 2.5mm spheres, primarily dark grey in colour, although some spheres were a lighter grey suggesting some non-uniformity in the impregnation and coating process.

X-ray Photoelectron Spectroscopy, or XPS, is radioactive composition technique on material surfaces. X-ray radiation of sufficiently high energy is beamed into the atomic level and will, dependent on binding energies, eject a photoelectron from the inner core. Since the binding energy of an entity is unique to itself, then this allows us to analyse both oxidation states and atomic composition. The technique is defined by;

$$\text{Kinetic Energy (KE)} = h\nu - \text{Binding Energy (BE)}$$

XPS therefore allows one to assess potential composition changes, in addition to the identification of the oxidation states, within the catalyst. XPS can be used in conjunction with Differential Scanning Calorimetry (DSC) which allows one to assess the mode of operation of a particular catalyst, or the mechanism of a particular reaction. This technique supplies different heat fluxes to sample and reference at constant temperature (isothermal) meaning that both samples stay at the same temperature. When a difference arises exothermic or endothermic conditions occur ($d\Delta H/dt$). To improve resolution of peaks sample masses of 5-10mg are used.

SEM can be used to give detailed information about surface morphology, topology and material surface composition, in particular building up an elemental map of varying elemental constituents in different regions of a particular sample. SEM is used in conjunction with X-Ray Diffraction (XRD) to determine the crystalline state of the structure, and with Energy Dispersive X-ray spectrometry (SEM-EDX) to do elemental mapping. The limitations on SEM-EDX are that it cannot pick out elements (lower than carbon in atomic number), it cannot give absolute quantities, and it has limited resolution to differentiate between elements with similar atomic numbers, although the species of interest here, Rh, Ir and O are sufficiently well separated on the periodic table.

SEM-EDX (using a Hitachi 3200 N SEM model) and XPS (using a VG Scientific XPS model) were used in this work to determine the degradation of the catalyst (in terms of the metal atoms lost) after a decomposition 'run'.

SEM-EDX mapping of individual elements in a Shell 405 catalyst sample before and after tests up to 750°C are shown in *Figure 4.2* below. The top left image in each mosaic represents what is actually 'seen' (in secondary electron mode), without any elemental data. The other micrographs show, clockwise, the concentrations of oxygen, iridium and aluminium, with brighter areas representing higher concentrations and darker showing deficient areas.

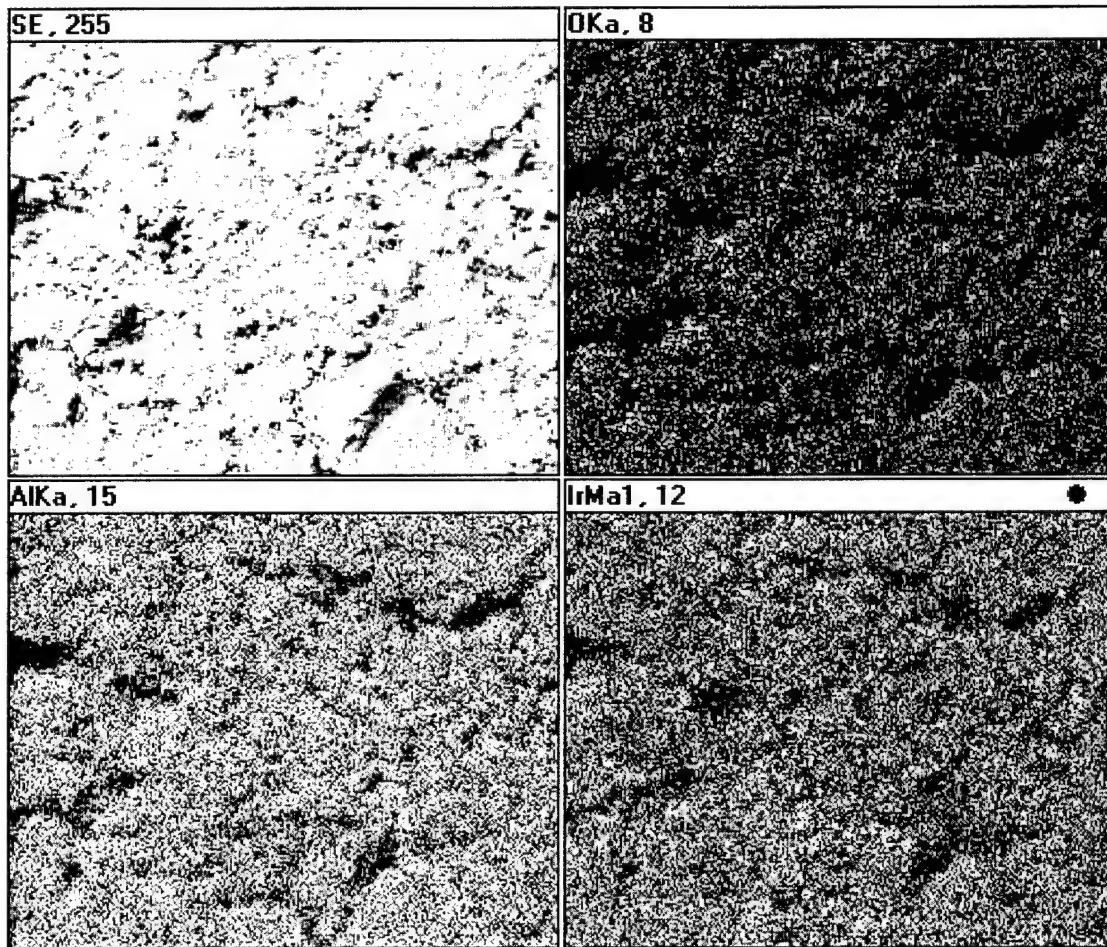


Figure 4.2: Scanning electron microscope image and elemental distribution maps of fresh Shell 405 catalyst

The as-supplied Shell 405 catalyst showed a very uniform dispersion of surface iridium, which is what would be preferred for a catalyst since the surface area of active metal particles is maximised.

In contrast, after reaction (*Figure 4.3*), the surface distribution was much less uniform, with the Ir appearing to have formed surface crystallites, probably iridium oxide. This corresponds well with the XPS results, which show that all metal catalysts were oxidised (electrons removed) after N₂O decomposition. Metal loss at the surface was found to be significant for the Shell 405 catalyst, but very small for the Rh based catalysts.

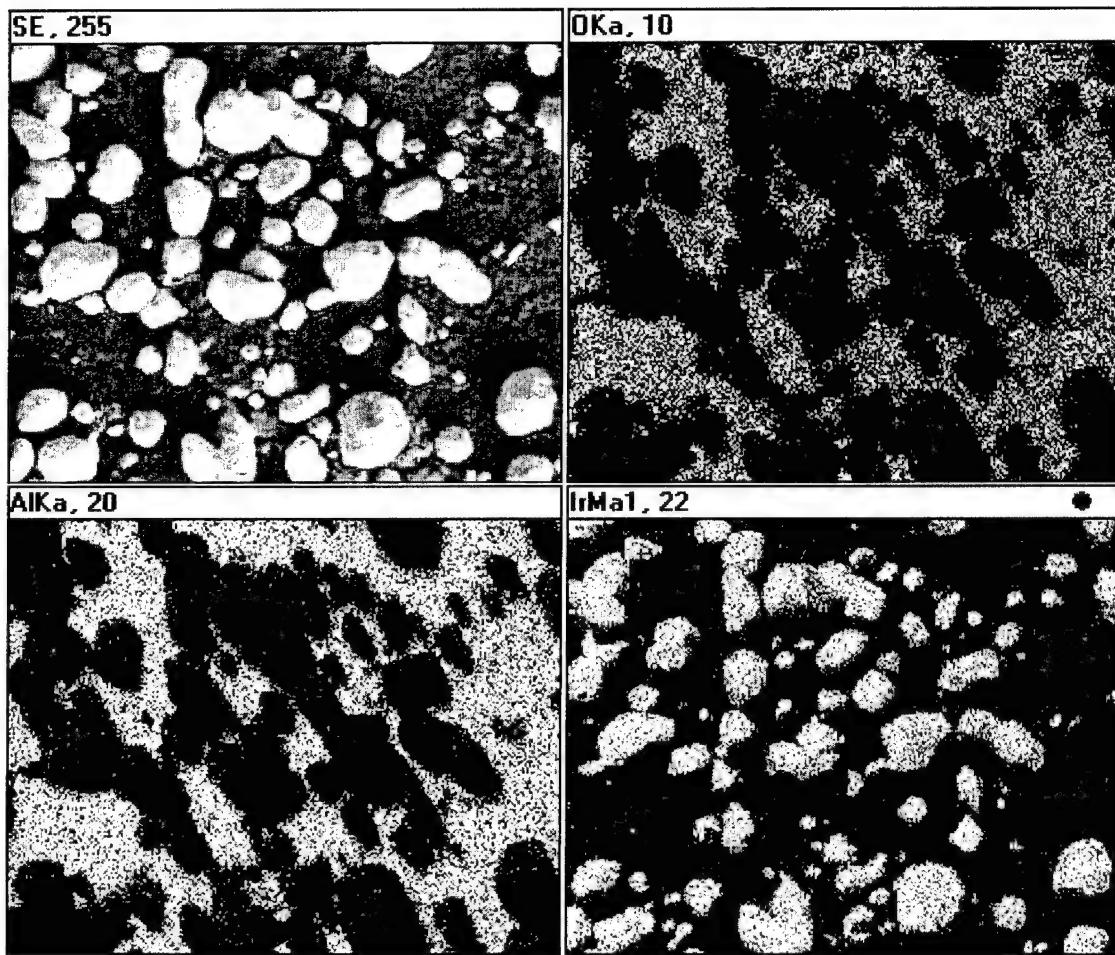


Figure 4.3: Scanning electron microscope image and elemental distribution maps of used Shell 405 catalyst

The following table compares the three catalysts characterised by XPS:

Catalyst	Atomic % metal before reaction	Atomic % metal after reaction	Oxidation state change
Rh/TiO ₂ (SG)	0.22	0.20	0 \Rightarrow +1
Rh/TiO ₂ on ceramic foam Al ₂ O ₃	0.23	0.20	+3 \Rightarrow +4
Ir/Al ₂ O ₃ – Shell 405	4.74	2.28	+1 \Rightarrow +4

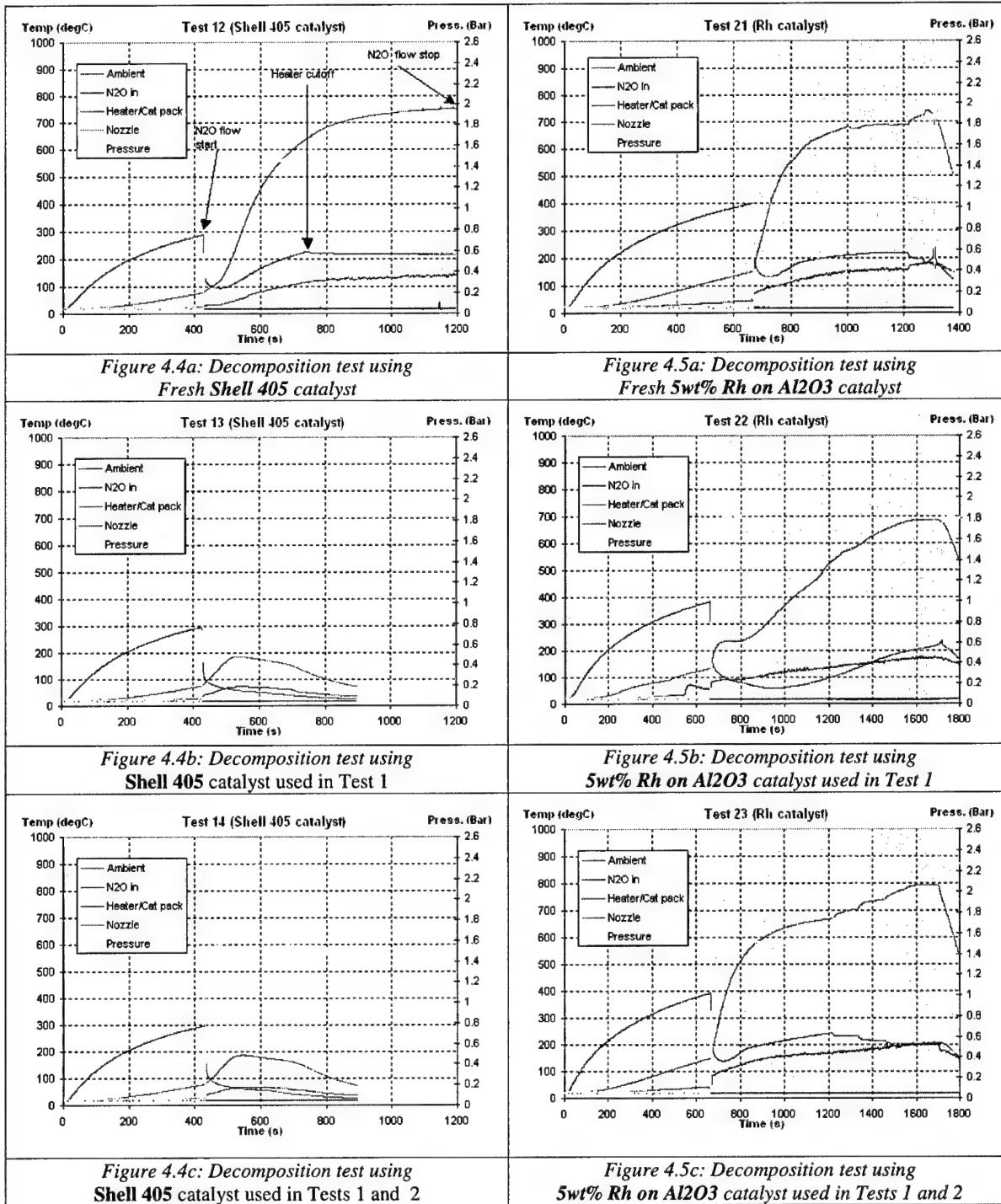
Table 4-2: Degradation of catalyst as measured by metal loss and oxidation state change

Funding limitations precluded SEM analysis of the 5wt%Rh on Al₂O₃ catalyst used for the majority of the tests.

4.4 Evaluation of catalyst degradation and restarts

4.4.1 Decomposition tests

Three tests were carried out using a single sample of ~15g of Shell 405. Conditions were as for earlier test runs, i.e. a flow control valve setting of 40, 4Bar indicated on the pressure regulator, 420s of heating time prior to flowing nitrous oxide and 645s (720s for first run) of total heating time. Data for these runs are shown in Figure 4.4 below, cross-referenced to the relevant test number in the Appendix A test matrix.:.



Figures 4.4a-c suggest that the Shell 405 catalyst is degraded by operation at a high temperature. Data for Tests 8-14 shown in Appendix A suggest that, for the experimental conditions given in Table 3-3, Shell 405 can withstand only one high temperature test (decomposition temperature $>750^{\circ}\text{C}$), corresponding to a throughput of 150g N₂O before degrading to the point where catalytic decomposition of N₂O is not possible. The N₂O throughput was 157g up to and including Test 1, 230g including Test 2, and 350g for Test 3.

Figures 4.5a-c show equivalent tests, for similar throughputs of N₂O but using Rh on Al₂O₃ catalyst (sample Rh-3). The N₂O throughput was 135g up to and including Test 1, 275g including Test 2, and 400g including Test 3. The catalyst does not degrade in the same fashion as the Shell 405, and subsequent tests on a fresh catalyst sample (Rh-4) showed that at least 500g throughput of N₂O is feasible with this catalyst before degradation. The decomposition temperature recorded at the nozzle end of the decomposition chamber was around 700°C in all three cases, similar to the temperatures recorded using Shell 405 catalyst. It is expected that these would be similar, since above $\sim 650^{\circ}\text{C}$ N₂O decomposes thermally and the heat from decomposition and the chamber walls is expected to sustain decomposition without the catalyst. For this reason the throughput of nitrous oxide is not a useful measure of catalyst effectiveness, since a thruster can in theory sustain an infinite throughput of N₂O once decomposition is initiated, as the subsequent heat generated thermally decomposes further N₂O without the need for the catalyst.

It is not clear why the length of time to reach 700°C decomposition temperature in the nozzle region in Test 22 using the Rh catalyst was 900s, significantly longer than the 300-500s in the other two tests.

4.4.2 Post testing catalyst structural analysis

Samples of the Rh catalyst fabricated by UniS-CD were submitted to MAST Carbon for microstructural analysis. The fresh catalyst was found to have an area of 202m²/g, consistent with a medium area gamma alumina. This is consistent with the substrate material used for deposition of the Rh.

After testing a number of the Shell 405 catalyst particles were found to have turned grey, which is consistent with the metal loss and surface morphology change noted by SEM, above. No change in overall morphology and size of the Shell405 was noted after testing..

The UniS-CD Rh catalyst particles also changed colour after testing, from an initial brown/grey colour to brown/white and after repeated use to a grey-white colour. The size of the particles also appeared to diminish, by $\sim 0.5\text{mm}$. This can be seen in Figure 4.6 below, the 4 Rh-catalyst spheres on the right, closest to the ruler comprise 2 full size (2.5mm Ø) brown/white spheres and 2 smaller ($\sim 2\text{mm}$ Ø) grey/white spheres:

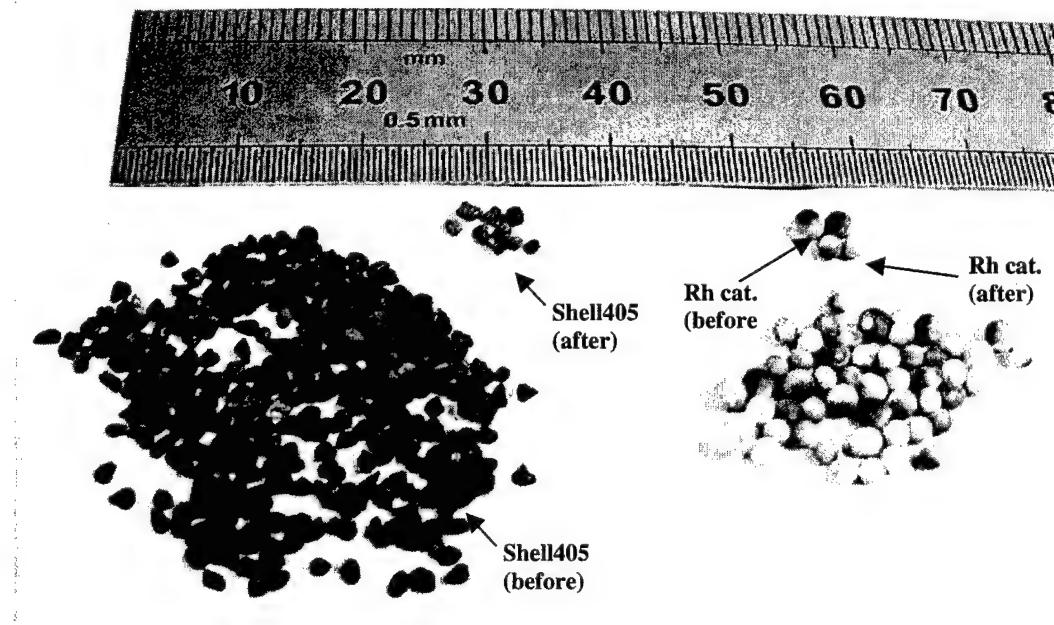


Figure 4.6: Catalyst visual comparison after firing.

The change in size of the Rh based catalyst, commensurate with a change in colour is particularly noticeable. It was also noted that the initial colour of the Rh catalyst was not uniform, some being black and others brown / grey, suggesting a non-uniform distribution of Rh on the surface after catalyst preparation.

The smaller, white/grey spheres were separated from the larger brown spheres in the used Rh based catalyst. The former was measured by MAST to have an area of $15\text{m}^2/\text{g}$ (compared to $202\text{m}^2/\text{g}$ for fresh catalyst) showing clear evidence for major structural collapse that could be responsible for the reduction in size. It is possible that the gamma Al_2O_3 has formed alpha alumina although this does require a high temperature, further evidence of effective decomposition of N_2O initiated by the catalyst.

5 ANALYSIS

5.1 Decomposition initiation

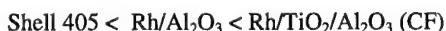
The Shell 405 catalyst successfully initiated decomposition of N_2O after heating for ~450s to a temperature of ~300°C, subsequently generating a measured temperature in the decomposition chamber downstream of the catalyst bed of around 750°C. This is very close to the 800°C suggested by Vadim Zakirov (Ph.D. thesis, University of Surrey, 2001), but is well below the adiabatic decomposition temperature of 1350°C which will should result from complete decomposition of N_2O . However damage to the spiral wound heater in Test 4, rated to 950°C suggested that a higher temperature than 750°C may have been generated. Temperature measurement downstream of the catalyst bed has also been shown not to accurately represent the actual decomposition temperature, as later results showed.

The research conducted by the University of Surrey chemistry department indicated that a catalyst comprised of Rh metal on sol-gel deposited TiO_2 on an Al_2O_3 ceramic foam (porous) substrate had a good potential for catalytically decomposing N_2O , as measured by the turnover frequency. In terms of activity at low temperatures the order of absolute reactivity was predicted to be:



This was principally due to the high concentration of metal on the surface of the Shell 405, around 36wt% Ir, compared to <5wt% Rh deposited on Al_2O_3 by the University of Surrey.

However in terms of decomposition rate per active metal ion (as measured by turnover frequency) then the order is reversed:



Initial efforts to fabricate a catalyst by metal deposition on a rigid ceramic foam block, which was assumed to be better form the point of view of handling and robustness, were not successful in initiating decomposition. This was partly due to not matching the block geometry to the decomposition chamber, but primarily appeared due to a fabrication error which resulted in ~10x less Rh than expected being deposited.

Subsequently a catalyst was manufactured using a gamma- Al_2O_3 substrate (in the form of 2.5mm diameter porous spheres, similar to those used by Vadim Zakirov in earlier research), on which ~5wt% Rh was deposited and impregnated into the pore structure.

The plots in *Figures 4.4 and 4.5* show that the 5wt% Rh catalyst on Al_2O_3 was successful in initiating decomposition of N_2O , when initially heated to ~400°C, some 100°C higher than the Shell 405. Given the higher intrinsic reactivity of Rh with N_2O compared to Ir in Shell 405, it is assumed that the lower metal content (5wt% v. 36wt%) and possibly the lower surface area due to the larger substrate size (2.5mm diameter spheres v. 1-2mm diameter particles in Shell 405) may have influenced the 'initiation' temperature. However accurate mapping of the boundary has not been carried out so this assertion is only qualitative.

5.2 Steady state operation

The temperature recorded downstream of the catalyst bed increased as N_2O pressure and hence flow rate were raised, up to 800°C was recorded for a feed pressure of 3Bar. However this is still well below the adiabatic decomposition temperature of nitrous oxide, around 1350°C. The question is whether decomposition is incomplete, and the adiabatic temperature is not being reached, or whether heat losses are preventing the true temperature from being read.

A thermocouple was therefore added to monitor the temperature in the centre of the catalyst bed, indicated by T4 in the schematic in *Figure 3.1*. Test 30, using catalyst sample Rh-4 recorded a maximum temperature of 1076°C, although the actual temperature may have been higher, as indicated in *Figure 5.1* below (the K-type thermocouple used was only rated to 1100°C):

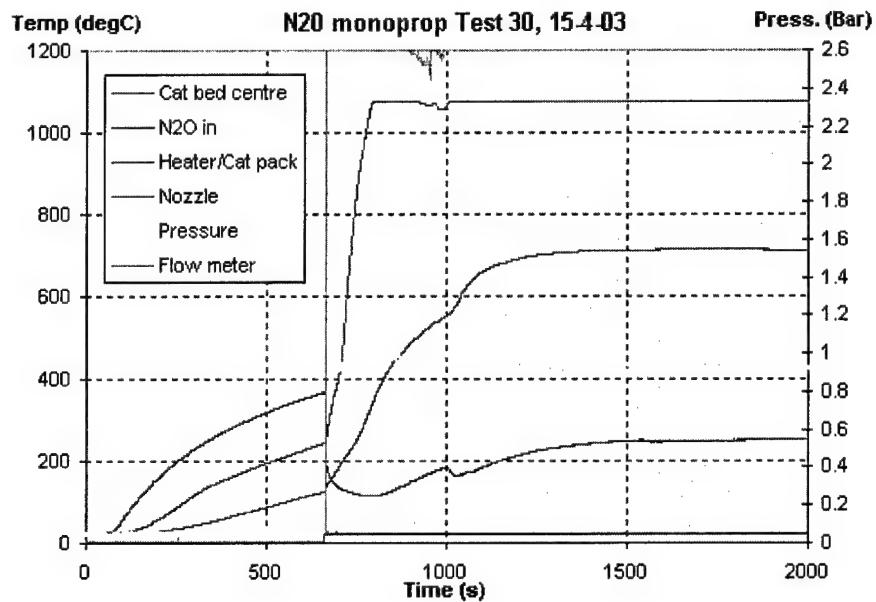


Figure 5.1: N₂O decomposition test using additional thermocouple sited in centre of catalyst bed (green trace)

Parameters for this test were as for previous tests, i.e. heat up time of 600s at 30W power followed by additional heating for 90s after the N₂O gas flow was started. The temperature recorded suggest that the catalyst initiated efficient decomposition of N₂O, and that heat losses from the insulated thruster were not significant. In this test, a total of 800g of N₂O were flowed through the catalyst, over a period of 7000s (115 minutes) giving a mean flow rate of 0.11g/s and the reaction was seen to be self sustaining, power to the heaters being cut after 600s.

5.3 Catalyst degradation

The XPS analyses suggest that the Shell 405 catalyst loses a substantial amount (almost 50%) of its active metal component, iridium (Ir), during one decomposition run. This is supported by SEM, which shows the uniform surface distribution of Ir changing to one where a number of dispersed crystallites, probably iridium oxide, are present. It is possible that during decomposition of N₂O, the liberation of free oxygen and/or oxygen oxidises some of the surface Ir with some additional quantity lost due to vaporisation, as suggested by XPS. Since the Ir based Shell 405 catalyst was designed for hydrazine, or N₂H₄, which produces NH₃, N₂ and H₂, but no free oxygen, its instability in a decomposed N₂O stream is unsurprising.

The analyses of how the catalyst chemistry changes were supported by tests in the laboratory at SSTL. Three tests on one sample of Shell 405, with an initial decomposition chamber temperature of ~750°C were followed by two tests where the decomposition temperature did not exceed 200°C. In effect, use of Shell 405 catalyst to initiate decomposition of N₂O is a 'one-shot' process, which denatures the catalyst and destroys its ability to further decompose nitrous oxide. On this basis, Shell 405 is not suited as a catalyst in a future nitrous oxide monopropellant thruster which would require a restart capability.

In comparison, RGA of the initial Rh based catalysts produced by the University of Surrey showed little or no loss of surface metal during extended nitrous oxide decomposition. In contrast, tests using the decomposition chamber at SSTL showed a limit of between 350 and 1150g of nitrous oxide prior to catalyst degradation. This figure was arrived at by considering test 30, in which decomposition was successfully initiated using a catalyst which had seen 350g throughput of N₂O, and test 31 and 32, where attempts to reinitiate decomposition with the same catalyst were not successful, indicating catalyst degradation. 350g-1150g N₂O throughput is greater than Shell405, where a nominal limit of 150g was indicated by test data, but is still short of the 3300-5000g desired in the specification (Table 3.1) to give a thruster impulse of 5-7.5kNs. But, because the nitrous oxide decomposition becomes self-sustaining after initial catalytic decomposition and heating of

the chamber, the value of N₂O flowed through the catalyst is not a particularly useful indicator of performance. The number of 'activations' before failure is more useful, since this gives an indication of the number of thruster restarts which could be obtained in a catalytic nitrous oxide monopropellant. In this respect the UniS-CD Rh-catalyst outperforms Shell 405. Given that the mechanism of catalyst degradation is probably a combination of thermal shock (causing structural collapse of the substrate) and oxidation of the active metal component, an accurate gauge of catalyst performance (survivability) would need to consider restarts and N₂O flow duration at operating temperature.

A typical specification for a hydrazine monopropellant thruster, such as manufactured by ARC UK or Snecma gives both a maximum number of continuous firings (with a maximum firing duration, thus indicating the propellant throughput limit), and a maximum number of cycles or pulses. An objective of further work would be to quantify thruster performance in both of these respects.

It should be noted that the above test results were obtained using an initial sample of catalyst produced with no attempt to optimise the fabrication route or decomposition chamber (thruster) design to minimise ill-effects on the catalyst bed. It is entirely possible that with additional catalyst research and thruster testing that performance could be improved to the level desired for a restartable N₂O monopropellant thruster.

5.4 Performance estimation

The decomposition chamber was not operated in vacuum, nor was thrust measured, hence an accurate value of Isp and thus the performance of the thruster cannot be made. However it is possible to offer an estimate of the performance based on the temperature recorded. Since exhaust velocity (and Isp) is proportional to the square root of absolute temperature, comparing the peak temperature recorded (1076°C, T4) with that predicted for full decomposition (1609K, or 1333°C, using the Isp code) shows that the exhaust velocity which could be generated is ~91.5% of the theoretical. Assuming optimal expansion of decomposition products using the given nozzle (with an expansion ration of 57.5:1) under vacuum conditions, this would indicate an Isp of ~164s, compared to the ideal value of 179s. This exceeds the Isp specification given in Table 3.1 of 150s, but would obviously need to be verified in practise.

However it can be stated that there is good potential for a restartable N₂O monopropellant thruster with an Isp in excess of 150s, using the Rh catalyst developed by UniS-CD. Further research would aim to optimise the catalyst performance and quantify and extend catalyst life and hence thruster operational life and restartability.

6 CONCLUSIONS

- Shell 405 (hydrazine monopropellant) catalyst, comprising 36 weight (wt%) percent iridium on an alumina particle substrate has been tested in a prototype nitrous oxide monopropellant catalytic thruster. Shell 405 is able to initiate catalytic decomposition of nitrous oxide after electrical resistance heating to approximately 300°C. A decomposition temperature of at least 750°C immediately downstream of the catalyst bed has been recorded, the actual decomposition temperature is likely to be higher (>1000°C) based on subsequent tests measuring the temperature in the centre of a Rh catalyst bed. The Shell 405 catalyst is rated to around 1100°C, the decomposition temperature of hydrazine. Exceeding this temperature, coupled with the free oxygen in the exhaust product stream is likely to have led to catalyst degradation.
- However the Shell 405 degrades after one high temperature test and cannot be reused. An approximate limit for the quantity of nitrous oxide which can be fed through a Shell 405 catalyst bed prior to degradation is 150g, equivalent to an impulse of 220Ns. Chemical and electron microscopy analysis has suggested that this degradation is due to iridium oxidation and loss from the catalyst surface, stemming from the high free oxygen levels in the products of decomposition of nitrous oxide. Free oxygen is not present in the products of decomposition of hydrazine, which the catalyst was designed to decompose.
- The University of Surrey Chemistry Department (UniS-CD) conducted an analysis of alternatives to iridium on alumina and determined that rhodium metal on an alumina substrate, on a direct comparison of metal content could offer an increased rate of nitrous oxide decomposition per metal atom of catalyst, and a reduced temperature / heat input for catalyst activation compared to Shell 405. Deposition of Rh on various ceramic substrates and residual gas (decomposition) analyses, in comparison with an earlier catalyst fabricated by the Surrey Space Centre resulted in a 5wt% Rhodium on (2.5mm spherical) alumina substrate catalyst, fabricated by a chemical impregnation process from a rhodium (III) chloride hydrate precursor. The effect of substrate and fabrication process on catalyst reactivity was not investigated in detail.
- Testing of this UniS-CD Rh catalyst in a prototype decomposition chamber showed that initial heating to 400°C to commence catalytic decomposition of N₂O was required. This is greater than the 300°C required for Shell 405 and is attributed to the lower metal content on the UniS-CD catalyst (5wt% compared to 36wt% for Shell 405).
- After catalytic decomposition was initiated, a steady state (thermal) decomposition temperature exceeding 1070°C in the centre of the catalyst bed was recorded at a feed pressure of 3Bar (4Bar absolute). This temperature implies an Isp greater than 160s, from theoretical calculations assuming operation in vacuum with a correctly expanded nozzle. Although this Isp value was not verified experimentally, it would have exceeded the original requirement for an Isp of 150s, and indicates the merit of further work on the concept.
- The UniS-CD Rh catalyst survived a throughput of at least 500g N₂O (at least 3x that of the Shell 405 catalyst) and multiple restarts (at least 5), unlike the Shell 405 catalyst. However the decomposition achieved for both Shell 405 and UniS-CD Rh catalysts was thought to be similar, particularly since decomposition becomes self-sustaining and does not require the catalyst once the temperature exceeds a temperature of around 650°C. The requirement was an impulse of between 5000 and 7500Ns, corresponding to a throughput of 3.5-5kg of N₂O. Therefore considerable further optimisation of the catalyst is still required before a proto-flight system can be built.
- Catalyst degradation is thought to be a combination of active metal loss, due to oxidation of the Rh, evaporation of Rh / Rh oxide from the catalyst surface and structural collapse of the alumina support.
- Development of a nitrous oxide monopropellant thruster shows some technical merit and is currently considered to lie between NASA Technology Readiness Level (TRL) 3, *Analytical and experimental critical function and/or characteristic proof-of-concept and TRL 4*, component and/or breadboard validation in laboratory environment.

RECOMMENDATIONS FOR FURTHER WORK

- Further work to develop the prototype nitrous oxide decomposition chamber and catalyst evaluated in this programme, towards a proto-flight demonstration thruster is recommended and would involve the following:
 - ◆ Catalyst improvements, including:
 - Analytical electron microscopy of the Rh catalyst before and after testing, to confirm the metal content (estimated at 5wt%) and to investigate the nature of the degradation from nitrous oxide decomposition products.
 - Increasing the active metal content of the Rh catalyst, from the estimated 5wt%, towards the 36wt% of the Ir based Shell405 catalyst. This would be with a view to reducing the catalytic initiation temperature from the 400°C established by testing to below 300°C, hence reducing thruster power requirements.
 - Increasing the contact area between the catalyst and the N₂O, either by grinding the metal / substrate combination, use of Rh powder or by deposition on a high surface area (ceramic) foam. Catalyst retention within the thruster when using a small particle size will need to be considered.
 - Evaluation of different substrate materials (Al₂O₃, TiO₂, etc.) and comparison of fabrication processes (sol-gel v. impregnation) to optimise catalyst active area, adhesion to substrate and general robustness.
 - ◆ Further decomposition chamber testing, including:
 - Establishment of the precise thermal conditions leading to N₂O catalytic decomposition
 - A chemical analysis of decomposed products from thruster, to establish the degree of chemical decomposition and (indirectly) the likely amount of heat loss from the thruster during operation.
 - Replacement of K type thermocouples (limited to 1100°C) with R-type or equivalent capable of measuring in excess of 1600°C (above the adiabatic decomposition temperature of N₂O).
 - ◆ Thruster tests
 - Improvement of the decomposition chamber design to maximise the efficiency of heating and minimise the catalyst degradation from contact with oxygen radicles formed during decomposition. Modification of the chamber construction to an all-welded design, as opposed to brazed, and possibly use of a higher temperature superalloy (e.g. Haynes alloy) rather than stainless steel for the chamber would ensure integrity for long duration testing. Testing catalyst durability for N₂O throughputs up to 5kg mass and multiple restarts (up to 50?) would be intended.
 - Establishment of a catalyst/thruster specification including number of thermal cycles (pulses) and maximum number of continuous firings with a maximum duration for each.
 - Testing under vacuum to investigate convective heat losses.
 - Construction of a thermal model of the thruster to evaluate heat losses.
 - Measurement of thrust in vacuum to directly calculate Isp, for comparison with inferred Isp from gas temperature measurements

An small scale programme of work would involve basic catalyst improvements and further decomposition chamber testing. A subsequent phase would entail more detailed thruster tests.

APPENDIX A: THRUSTER TEST MATRIX

Test Date	Log-1000 Fester No.	Temp. °C	Seg-1000			Xc-Second			Xc-Third			Xc-Fourth			Xc-Fifth		
			Setting [3a-2]	Setting [3a-2]	Setting [3a-2]	Trac-1 Time [3a-2]	Trac-1 Time [3a-2]	Trac-1 Time [3a-2]	Trac-2 Time [3a-2]	Trac-2 Time [3a-2]	Trac-2 Time [3a-2]	Mean Dwell Time [3a-2]					
1 03/05/01	16	26	40	2	200	40	235	290	55	104	115	1.05	1.05	1.05	1.05	1.05	
2 03/05/01	15-6	26	40-5	2	420	50	355	460	55	115	115	1.05	1.05	1.05	1.05	1.05	
3 23/05/02	16-8	26	40	2	420	515	50	555	55	107	115	1.05	1.05	1.05	1.05	1.05	
4 21/05/02	16	26	40	2	420	515	55	714	55	118	115	1.05	1.05	1.05	1.05	1.05	
5 22/05/02	17-30	38	40	2	420	50	350	350	55	115	115	1.05	1.05	1.05	1.05	1.05	
6 22/05/02	17-30	38	40	2	420	50	350	405	55	115	115	1.05	1.05	1.05	1.05	1.05	
7 22/05/02	15-30	38	40	2	420	1015	355	115	115	115	115	1.05	1.05	1.05	1.05	1.05	
8 22/05/02	2	26	40	2	420	50	350	394	55	104	115	1.05	1.05	1.05	1.05	1.05	
9 27/05/02	22	38	40	2	420	510	53	303	15	115	115	1.05	1.05	1.05	1.05	1.05	
10 23/05/02	22	38	40	2	420	510	54	644	293	115	115	1.05	1.05	1.05	1.05	1.05	
11 23/05/02	25	38	40	3	460	30	555	293	115	108	115	1.05	1.05	1.05	1.05	1.05	
12 23/05/02	25-52	38	40	3	420	750	75	293	115	115	115	1.05	1.05	1.05	1.05	1.05	
13 23/05/02	26	38	40	3	420	30	132	297	115	313	115	1.05	1.05	1.05	1.05	1.05	
14 23/05/02	27	38	40	3	420	30	135	293	115	313	115	1.05	1.05	1.05	1.05	1.05	
15 02/07/02	37	38	40	3	180	240	45	300	114	115	115	1.05	1.05	1.05	1.05	1.05	
16 02/07/02	37	38	40	3	180-120	180	20	115	115	115	115	1.05	1.05	1.05	1.05	1.05	
17 02/03/02	28-39	38	40	2	216	450	134	285	115	115	115	1.05	1.05	1.05	1.05	1.05	
18 02/03/02	28-39	38	40	2	360	510	212	303	193*	115	115	1.05	1.05	1.05	1.05	1.05	
19 02/03/02	28-39	38	40	1	360	510	212	303	193*	115	115	1.05	1.05	1.05	1.05	1.05	
20 03/03/02	35	38	155	2	260	30	75	403	1	115	115	1.05	1.05	1.05	1.05	1.05	
21 03/03/02	35	38	155	2	260	30	145	403	36	115	115	1.05	1.05	1.05	1.05	1.05	
22 25/03/02	35	38	155	2	260	30	632	383	1	115	115	1.05	1.05	1.05	1.05	1.05	
23 23/03/02	22	38	155	1.5	260	30	734	392	31	117	132	1.05	1.05	1.05	1.05	1.05	
24 23/03/02	35	38	155	1	300	750	751	307	31	115	115	1.05	1.05	1.05	1.05	1.05	
25 23/03/02	34	38	155	1	300	750	187	263	1	115	115	1.05	1.05	1.05	1.05	1.05	
26 23/03/02	34	38	155	1	300	350	135	275	15	314	115	1.05	1.05	1.05	1.05	1.05	
27 15/11/02	36	420	510	1	420	510	131	275	15	314	115	1.05	1.05	1.05	1.05	1.05	
28 15/11/02	36	38	155	1	300	775	774	357	355	115	115	1.05	1.05	1.05	1.05	1.05	
29 03/11/02	36	38	155	1	300	750	75	353	355	115	115	1.05	1.05	1.05	1.05	1.05	
30 15/05/03	38	38	155	1	300	320	1076	363	4	21	80	1.05	1.05	1.05	1.05	1.05	
31 23/05/03	40	38	155	1	300	320	335	363	15	115	115	1.05	1.05	1.05	1.05	1.05	
32 23/05/03	40	38	155	1	300	750	475	365	15	115	115	1.05	1.05	1.05	1.05	1.05	